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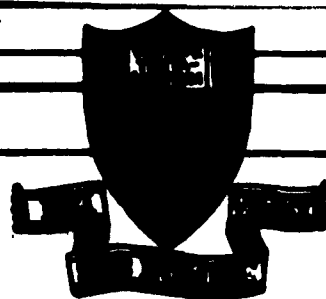
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THE PHYSICO-CHEMICAL ASPECTS OF
ORGANIC SEMICONDUCTORS

H. A. Pohl

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THE PHYSICO-CHEMICAL ASPECTS OF ORGANIC SEMICONDUCTORS

ABSTRACT

The result of experiments on organic semiconductors is compared with existing theory and it is found that there are certain aspects of the electronic behavior of both monomeric and polymeric semiconductors prepared from organic materials which need considerable enlightenment. As this study points out, there are major problems such as in explaining the origin of the activation energy observed for the conduction processes, in explaining the puzzlingly high conductivities of incompletely crystalline materials, and in explaining the low sensitivity to impurity (and possibly to morphology) exhibited by large numbers of organic semiconductors. This paper summarizes the present experimental and theoretical positions and suggests areas of attack.

At present, in comparing the organic semiconductors with the best examples of the inorganic ones, it should be noted that while overall conductivities for either class of material can be made quite large and comparable with the conductivities of some metallic substances on the one hand, on the other hand the organic semiconductors have not as yet been prepared with the high mobilities characteristic of the highest quality inorganic semiconductors. This presently seriously proscribes the usage of the organic semiconductors. However, there appear to be certain attributes of the presently available organic semiconductors which may offer some advantage over the presently available inorganic semiconductors. The high pressure sensitivity of certain organic resistors, for example, may be an example of this.

THE PHYSICO-CHEMICAL ASPECTS OF
ORGANIC SEMICONDUCTORS

by

Herbert A. Pohl

Princeton University Plastics Laboratory

Work on organic semiconductors appears to have started with the observation by Pocchetino¹¹⁹ of photoconduction in anthracene. Dark conduction seems to have been observed by Koenigsberger and Schilling⁷⁷ somewhat later. The subject lay dormant until researchers were spurred in 1941 by the suggestion of Szent-Gyorgyi¹⁴⁴ that our understanding of some biological processes would be increased if we viewed certain protein structures as having attributes of semiconductors. He later offered some proof of this contention by showing that dyed proteins could act as photoconductors^{143, 145}. Vartanyan¹⁵²⁻⁷ and Eley and coworkers³⁰⁻⁶ in the late forties began an intensive study of the semiconducting properties of organic compounds, especially on the phthalocyanines. Since that time there has been strong activity in the field of organic semiconductors, especially dealing with matters of structure, behavior, and the causes. At no time since the clear predictions of Szent-Gyorgyi have overtones ceased to be heard as to the importance of electronic transport of energy in biological processes. Evans and Gergely³⁸ suggested, for example that the hydrogen bridges at the amide links of the polypeptides would furnish a source and path of conduction electrons whereby energy could be moved from one site to another in living cells. Nelson¹⁰⁹ observed photoconduction in chlorophyll preparations. Riehl¹³³ and Eley³⁶ have observed dark conduction in proteins. It may be inferred from the

suggestive theories of Katz⁶⁴ and of Bradley and Calvin¹⁵ as to the role of semiconduction in photosynthesis, as well as from the studies by Mason⁹⁹ and others on carcinogenic activity as related to the energy band characteristics of aromatic hydrocarbons, that the interest of biochemists and biophysicist will be high in this area.

In the following discussions we shall be restricting our attention to organic materials which conduct electronically and homogeneously. We shall, then, not include discussion of materials which conduct ionically (electrolytically), nor shall we include materials which are mechanical mixtures of insulators and conductive fillers⁹⁸. For the purpose of this discussion we shall class^a/material as a semiconductor if it generally fits the following attributes:

- (i) Exhibits a specific conductivity roughly in the range 10^4 to 10^{-12} mho cm^{-1}
- (ii) Exhibits a negative temperature coefficient of resistivity.
- (iii) May exhibit a conductivity highly sensitive to impurity and morphology
- (iv) May show a high thermoelectric power, one which might be either positive or negative with respect to a given metal with which it is in contact
- (v) Exhibits rectification or at least non-ohmic behavior at junctions
- (vi) Exhibits photosensitivity, perhaps as a photovoltage, or as an increase in conductivity upon being illuminated.

NATURE OF CONDUCTION IN ORGANIC SEMICONDUCTORS

Electrical conduction can be regarded as involving three factors; the number, the charge, and the mobility of the current carriers. In organic materials it is very probably

the unit of electrical charge which moves. This leaves as unknowns the source and mobilities of the carriers. As will be seen, there are still formidable problems remaining as to just how the requisite ionization to form carriers can occur in organic materials. There is no less a problem in explaining the nature of the mobility processes, the movements of the electrons (or holes) from molecule to molecule. Indeed, the presence of anisotropy in the mobilities is perhaps more marked in the organic material, pyro-graphite, than in any other semiconductor.

In terms of conventional band theory, the existence of a partly filled band is a precondition for semiconduction. Closeness of the quasi-continuous level spacings is considered to be developed by the overlapping of the atomic orbitals and is often treated in terms of a tight binding or orthogonalized plane wave analysis of the wave functions. In molecular solids i.e. solids containing appreciable fractions of the atomic separations having the dimension of van der Waals distances, overlapping of the orbitals is generally restricted not only to the individual crystal as in elemental semiconductors, but to just a few atoms. Most organic semiconductors are molecular solids. The limited overlap of the orbitals due to the interference offered by the presence of large gaps such as the intermolecular distances should greatly reduce the fuzzing out of the sharp energy levels of the lone molecules. As a result there will be numerous narrow bands, rather than few wide ones. Transitions between energy states will be limited by the restricted number of available states, and by the relatively large size of the energy spacings as compared with thermal energy. Fully occupied bands, and little dark conduction will therefore be expected in most organic substances. This statement should apply to both saturated and to aromatic compounds. The π electrons of substances of aromatic character, such as benzene, ferrocene, anthracene,

etc., may be considered in a zeroth order approximation to form a half-filled zone or energy band, but with wide spacings between successive levels.

It has been said that the aromatic carbon compounds having less than one electron per carbon atom should be viewed as systems filling only parts of a band, and therefore as possessing a kind of superconductivity along the conjugated chains. This cannot be the case in those molecules containing even numbers of electrons in the lowest energy states in the absence of external fields (benzene, e.g.) for these electrons are paired degenerately (or very nearly so) in each state. The attachment of electrodes to the conjugated rings, if this were possible, would not result in superconductivity. Rather, it is to be expected that only in molecules containing high densities of excited states, or of unpaired electrons, would appreciable conductivity be observable¹²⁷. During 1961 significant advances have been made in the application of quantum mechanical techniques to the problem of conduction in organic materials. Mette and Pick¹⁰² had shown in 1953 that the conduction in anthracene was anisotropic. This was confirmed by the more recent work of Kepler⁷¹ and of LeBlanc⁸⁹. LeBlanc has shown by quantum mechanical arguments that one can account rather satisfactorily for the anisotropy, and qualitatively for the magnitude of the mobility. It now seems to¹⁰² rather well shown that the source of carriers in the small aromatic hydrocarbons, such as anthracene and other good insulators, must be essentially external. One must either inject carriers at the boundaries such as done in the experiments of Moore and Silver¹⁰⁴ using chemical solutions, or by photoexcitation²⁴ in order to have appreciable currents carried by the material. It is possible for the injected electrons or holes in an organic insulator like anthracene to experience transport in either of two rather different mechanisms. Transport may occur by what may

be described as 'hopping' processes, or else by a grander 'wave packet drifting' process, describable by simple band approximation approach. In hopping processes one generally sees low mobilities (less than $1 \text{ cm}^2/\text{volt-second}$) which obey an exponential temperature dependence. In the wave-packet-drifting type the mobilities are generally larger than $1 \text{ cm}^2/\text{volt-second}$, and depend less drastically on temperature, in a manner such as $T^{-3/2}$ or $T^{+1/2}$, etc. On applying the band treatment to anthracene, LeBlanc found it to be valid upon applying criteria based upon the observed mobilities and uncertainty principle arguments such as given by Frohlich and Sewell⁴³. In order for such band approximations to be physically meaningful, stringent restrictions are set by the uncertainty principle. One way to state this is that the mean free path of the carriers, with respect to their being scattered, must be rather greater than the lattice spacings. If this is not true, then Bloch functions will be poor approximations to the proper wave functions describing the carriers.

On applying this restriction in the formulation given by Frohlich and Sewell, LeBlanc⁸⁹ concluded that the observed mobilities are consistent with the band description only if the band widths for holes or electrons are of the order of, or less than, kT at room temperature. His detailed calculations using Hueckel linear combinations of Slater type atomic orbitals in a tight binding approximation showed the one electron band which was appropriate to excess electrons and holes to be highly anisotropic and to have a width of about $kT/2$ as required. There is still remaining the problem of accounting for the mobility quantitatively, but this is complicated by the difficultly calculable effects of induced lattice distortions in the vicinity of the hole or electron (i.e. polaron formation). Carriers moving at low enough velocities tend to become self-trapped by the distortion^{41, 115}.

One therefore expects to see a rather sharp transition between the two types of transport. Some evidence for this sharpness of transition may be drawn perhaps from the comparison of the conductivity ratios for crystal versus melt of the same semiconductors as shown in Fig. 1. As Pohl¹²⁷ noted, there are two rather sharply defined regions to be seen, one enclosing the materials of high, the other enclosing the materials of low mobility, probably describable as fitting the wave-packet-drift and the hopping types of transport respectively.

It might be noted in passing that the data collected so far as shown in Fig. 1 pose a considerable problem for the theorists. The band approximation has been spectacularly successful in the interpretation of semiconduction and related electronic properties of certain solids. One of the principle tenets of the theory, however, is the presupposition of a high degree of order in the solid. It must not be presumed, however, that a sort of converse exists, and that one can expect that only those materials having a high degree of order do show appreciable semiconduction. The data¹²⁷ of Fig. 1 is strong evidence that semiconduction is often either little affected or is even strongly increased by a great loss of order, such as in the conversion of a single crystal to the liquid state which is only a short distance away temperature-wise. Some help in resolving this problem may come in the future by calculations such as those of Eisenschitz and Dean²⁹ who showed that energy bands may be considered to occur in the liquid state. Their calculations were made for chains of atoms having nearest neighbor distances as random variables, and used the tight binding approximation. They concluded that the conductivity properties of metallic potassium and the insulating properties of argon would persist in the liquid state, after observing that the general features of band distribution and overlap were preserved. Clearly, further experimental and theoretical

study of electron transport in liquids and amorphous materials is desirable.

In addition to the contributions to our understanding of electron transport processes in the insulator materials such as anthracene just described, important insight into conduction processes in the more highly conducting organic materials appears to have been made recently. Kepler, Bierstedt and Merrifield⁷² recently reported on a set of organic salts which conduct well. These salts are based on tetracyanoquinodimethane (TCNQ) which forms radical ion salts with bases. These molecular crystals consist of strong electron donors and strong electron acceptors in a highly ordered array. Menefee and Pao¹⁰¹ have carried out molecular orbital calculations for the crystal of triethylammonium: (tetracyanoquinodimethane)₂ ion radical salt. Good agreement was obtained on calculations of the activation energies of electron conduction and magnetic susceptibility, using the LCAO method combined with a crystal field splitting scheme. The results indicated that there would be a splitting of the ground state into two levels separated by 0.12 eV (corresponding to the forbidden gap separating the filled and unfilled levels) and with the ground level further split in two to the extent of 0.003 eV (corresponding to a magnetically observable activation energy), and the upper level remaining degenerate.

In another well clarified case, that of the superpolymer, graphite, the band structure and electronic properties have been studied in a penetrating and very satisfactory fashion based upon ab initio calculations employing wave mechanics. The conductivity of graphite decreases with increasing temperature. It is therefore to be considered a metal even though the lattice structure and type of bonding (partially van der Waals) resembles that familiar in semi-

conductors. Three coplanar bonds hold each atom to two others to form planar layers of atoms. The layers are separated by a spacing typical of molecular crystals, about 3.35 Å. This large spacing and the weak inter layer force resulting from it permits the inter-layer penetration of many types of foreign substances to form interstitial compounds^{28,53-6}.

The energy contours in momentum space have been calculated by several investigators, notably by Wallace¹⁵⁹, Coulson²⁵, Corbato²⁴, and by Slonczewski and Weiss¹⁴⁰. A typical Brillouin zone of graphite⁵⁷ is shown in Fig 2. This calculation applies only to single crystals of graphite which are free of internal defects and stacking faults. The energy of the filled bands is highest very near the edges HK of the zone, which causes the zone to be filled with electrons up to an energy surface of rather complicated shape surrounding the edges HK. This constant energy surface formed from the portions in each corner is shown in some detail in Fig. 3. The surface of constant energy bulges beyond the zone edge at the top and bottom, e.i. close to points H and K. Near H and K the ellipsoidal portions therefore contain electrons, while the center ellipsoid contains holes. The surface shown, it should be pointed out is not the end result of an exact calculation, but is rather a representation of one of the more likely surfaces selected from among many possible ones which one obtains from group theoretical considerations. The selection of the particular contours has been determined experimentally, particularly by work on the magnetic susceptibility, especially the de Haas-van Alphen periodicities, as by McClure⁹⁵ and by Soule¹⁴¹ or cyclotron resonance measurements⁸⁷ by Lax and Zeiger. In terms of carrier concentrations and effective masses for carriers moving parallel to the layer planes, one obtains:⁵⁷

	<u>electrons</u>	<u>holes</u>
Carrier concentration (number per atom)	2.3×10^{-5}	2.1×10^{-5}
Carrier effective mass	$0.036 m_e$	$0.07 m_e$

Paramagnetic resonance¹⁵⁸ and cyclotron resonance measurements⁴⁵ have confirmed this theory for graphite which now appears to be in an excellent state of advance.

Having looked at the several recent advances which have been made in the application of quantum mechanics to specific cases of organic semiconductors let us now turn to the more general problem of how conduction may be understood to occur in the entire class of organic materials. There are several puzzling features about the electronic behavior of organic materials which prompt questions as the propriety of applying the simple band theoretical model in all cases. Among others, three principal problems are:

- (1) The proper evaluation of the process whereby the carriers could be considered to arise.
- (2) The interpretation of carrier mobilities in cases where the mean free path is low^{58, 64}
- (3) The interpretation of effects of gross disorder or impurity.

In the first place, the production of carriers in an organic material implies the generation of separated ions, whether by injection or by internal thermal excitation processes. In view of the fact that the (vapor phase) ionization energy-electron affinity difference for most organic molecules of aromatic character is about 7 eV or higher it appears quite difficult to arrive at energies of 0.7 eV or less generally observed as the apparent activation energy, E_a , for conduction.

In the second place, the observed mobilities for most organic materials as determined so far are low i.e. less than

$2 \text{ cm}^2/\text{volt sec.}$, and are often several orders of magnitude smaller. The interpretation of such mobilities as due to hopping processes would seem to infer an additional energy of activation term due to the activation energy for hopping. This would seem to increase the difficulties of interpreting the observed small activation energies¹²⁷.

In the third place, it appears that in many organic systems the effect of gross disorder or impurity is unexpectedly small, or even in the wrong direction, at least in terms of a simple band model¹²⁹.

Riehl¹³¹, in a penetrating series of experimental studies observed that the activation energies of solid insulators was in the order of magnitude of 0.7 eV, and suggested that the formation of carriers took place stepwise through the formation of nearest-neighbor ion pairs which later dissociated to form the carriers. Eley³⁰⁻⁶ and co-workers studied many organic systems, monomeric and polymeric, and evolved an interesting theory in which conduction was pictured to result as the passage of an electron from one excited state of a molecule to another by means of tunneling, and identified the activation energy for conduction $E_a = E_g/2$ with $1/2 E_{\text{opt.}}$, where $E_{\text{opt.}}$ is the energy for optical excitation to the lowest excited state. They used the electron-in-a-box model of Kuhn⁹², Bayliss⁸ and of Simpson¹³⁹ (W.T.) to estimate the allowed electron states of conjugated molecules.

McConnell⁹⁶⁻⁷ derived the transition probabilities for electron transfer between molecules, and it is apparent that such considerations will be important in the proper understanding of electron mobility in conducting aromatic molecular crystals. He pointed out that the self-trapping energy for intramolecular trapping of electrons in flight can be expected to be inversely proportional to the number of contiguous aromatic C-C bonds. To this extent the activation energy for resonance transfer of electrons can be expected to decrease

with the increase of size of aromatic molecules. Yamashita and Kurosawa¹⁷⁶ made similar calculations for the self trapped positive hole carriers in NiO. Trlifaj¹⁴⁸ considered the motion of self-trapped excitons in molecular crystals.

Lyons⁹² has made a study of the photo- and semi-conduction in organic crystals, using quantum mechanical considerations. The excited electronic states of a molecular crystal can be portrayed, following the usual arguments, in a number of ways. Dynamically, there can exist neutral excitation waves resulting from the passage of excitations sufficient to produce only neutral, but excited molecules. There can exist ionized excitation waves wherein nearby molecules have lost and gained electrons pair-wise. Finally, there can exist the completely ionized states where the electrons have been removed to large distances from the parent molecule. Here the motion of the electron is independent of the motion of the hole, and Bloch functions can become appropriate descriptions of the system. Precise calculations of the above systems by quantum mechanical methods is quite difficult, and one resorts to approximate classical and quantum mechanical procedures. Lyons compared the energy, I , needed to ionize a ground state molecule of a crystal with the energy, I_g , of ionization in the gaseous state. He estimated the polarization energy, W , of an ion in the crystal of either naphthalene or anthracene, as $W = -\frac{1}{2}ae^2/S_1^4$, where a is the polarizability, e , the electronic charge, and S_1 is the separation of the ion from the neutral molecule neighbor. Using $I = I_g - 2W$, he finds $I = 7.2 - 2(1.0 \pm 0.3) = 5.2 \pm 0.6$ eV for anthracene and $I = 8.1 - 2(0.8 \pm 0.3) = 6.5 \pm 0.6$ eV for naphthalene. The energy to produce photoemission would be expected to be $I - W$, i.e. 6.2 eV for anthracene and 7.3 eV for naphthalene. This checks rather well with the observed value (2200 Å) for anthracene photoemission.

Lyons also considered the familiar picture of large hydrogen-like (Rydberg) orbitals in which the excited electron is occupying orbitals of large radius encompassing several neighboring sites. Ionized exciton states were also considered in which pairs of ions on neighboring molecules were involved.

An important point is that quantum mechanical "mixing" of electronic states can occur. Mixing of the two lowest neutral exciton states has been discussed and observed^{16,27}. Furthermore, all ionized exciton states of the same crystal symmetry as neutral states must mix with them, with the consequence that neutral states are partly ionic and vice versa. This results in the expectation that one should see the physical increase of probability of transition to ionized states from neutral states. At the more highly excited 'Rydberg' levels, the orbitals would be expected to overlap strongly with orbitals of neighboring molecules. This opens a way for one to explain that free-electron conductivity may arise among the more highly excited exciton states.

In comparing the observed energy gap, E_g , of semiconduction for various aromatic hydrocarbons with the estimated height of both the lowest ionized state and also with the energy of the molecular triplet level, Lyons observed a close correlation, especially between the triplet level and the energy gap defined by the equation $\sigma = \sigma_0 \exp(-E_g/2kT)$. This poses the problem mentioned earlier. It is not clear from Lyons' rather careful analysis just why it is that it is the triplet level rather than the ionization level which should be related to E_g . When the lowest ionized level lies above the triplet, formation of the triplet states is not sufficient to produce ions, therefore some auxiliary mechanism must be called for. If only a thermal mechanism operated for the production of carriers, then there seems to be little reason for the triplet level to be indicated by the energy gap.

Wilk¹⁶⁶ has also considered this problem in considerable experimental detail. For linearly arranged aromatic ring hydrocarbons, for example, Wilk observed that the activation energy for conduction, E_L , was $E_L = (17 - n)^2/100$, for $n = 1$ to 5 linearly hooked aromatic rings, a relation fitting observation to $\pm 5\%$, except for bent compounds like pyrene, coronene, rubrene, or 3,4 benzpyrene. He suggests one might expect metallic conduction at $n = 17$.

O. Simpson^{112,137,138} has studied the electronic properties of aromatic hydrocarbons, especially the diffusion of excitons upon photoexcitation. The general problem of the motion and mobility of the carriers in organic molecular solids remains unsolved⁴⁰. It appears likely that there will be successful attacks made in the near future. Gross⁴⁷ discussed the self-trapping of slow electrons, agreeing generally with the earlier conclusions of Landau (1933) and of von Hippel (1936, 1940) that such self-trapping can exist, and suggesting reasons around why Frohlich, Pelzer, and Zienau⁴² concluded that it would not. Joffe cites⁶⁴ considerable evidence from the Russian literature⁴⁸ on inorganic semiconductors to deduce that hopping processes, having exponential temperature dependence, does exist. The problem of whether or not a Hall effect would be measureable for carriers moving by hopping has been argued¹⁷³. Balkanski⁷ and Haken⁵⁰ have presented equations describing the rate of annihilation and emission of photons to create moving excitons in semiconductors. The polarizations of electronic transitions in aromatic hydrocarbons and their mono- and divalent ions have been examined⁶⁰.

In dealing with the electron mobility in biological systems, Mason⁹⁹ showed that one could find a correlation between the ability of a compound to initiate carcinoma and their ease of promotion from the ground state.

THE RESULTS OF EXPERIMENT

In discussing the electronic characteristics of various organic materials, we shall proceed in order of discussion from the small to the large in molecular size. We shall discuss first the small, monomeric molecules, then the polymers. Among the polymers we shall consider first those formed by coordinated covalencies (i.e. the complexes) then those formed with regular covalent bonds, and finally those formed with ionic bonds between the monomeric portions.

To date, all substances examined appear to obey a conductivity-temperature relation describable by Fermi-Dirac statistics (which reduces mathematically to exponential behavior at low conductivities), although there are numerous examples where the plot of log conductivity versus the reciprocal of the absolute temperature shows 'breaks' indicating changes of dominance in the mechanism as the temperature passes from one regime to another.

It is interesting to note that organic compounds made principally from C,H,O,N. and possibly certain other elements such as P,S,Cl,Br,I, etc., can exhibit a tremendously wide range of conductivity. Organic materials, especially the polymers, can exhibit conductivity up into the semi-metallic range, 10^3 to 10^4 mho/cm, and one can now rather at will produce organic materials having any resistivity from there on down to that of the best known insulators, 10^{-22} mho/cm or so. This gives a range of 26 orders of magnitude, a truly large range of values for a physical quantity, and leaves much room for experimental changes. It is generally customary to regard the conductance range from 10^3 mho/cm or higher as the 'metallic' range, that from 10^3 to 10^4 as the semi-metallic, that from 10^3 to 10^{-12} as the semiconductor, and that from 10^{-12} to 10^{-22} or higher as the insulator range.

Measuring Techniques

As judged from prior work on germanium, silicon, and similar inorganic semiconductors, it would appear that purity and morphology should be most important variables in the study of organic semiconductors. This seems to be borne out in the case of the highly conductive ionic polymer radical salts, but seems not to be critically important in many other instances. The matter is still under active investigation. Purification may be carried out by extraction, crystallization, sublimation, chromatography, or in some cases, by zone refining. For the case of polymeric semiconductors it is usual to be limited to the use of pure starting materials, careful synthesis, followed by extractive, precipitative, and rarely, chromatographic or zone refining techniques.

The materials investigated so far have been single crystals, powders, compacts, and melts. There are decided theoretical advantages at present in the interpretation of results on using single crystals. In work with compacts of organic crystalline material it had been reported that pressure effects ceased to be important above about 80 atmospheres^{1, 31}. However, work by Pohl and Opp¹³⁰ with certain eka-conjugated polymers showed that at pressures up to 60,000 atmos. the resistivity was still a strong function of pressure. Examination of the conductance of organic materials in the form of films formed by evaporation or other means is frequent. In all cases whether on examining crystals, polycrystalline compacts, films or other solid or semi-solid forms, there exist three major causes for ambiguity in the results. Interpretation of the results is complicated by the existence of anisotropy, of interface effects, and of competing surface versus bulk electronic properties. Progress has been made in the interpretation of results on porous or inhomogeneous media.^{52, 67, 146}

In the actual measurement of the electronic characteristics of semiconductors, it is often observed that specific electrode effects exist which complicate matters. As a con-

sequence, it is preferable to measure conductivity, for example, by a 'four-point' probe technique rather than using somewhat more direct methods prone to errors due to unwanted emf's at electrode interfaces.

ELECTRONIC PROPERTIES OF ORGANIC MATERIALS

The Simpler Organic Molecules

There has been intense work done on the study of the electronic properties of the simpler organic molecules. Naphthalene and anthracene^{71,102,132} considered as models of pure aromatic compounds, have been especially studied with somewhat conflicting results. This is due in large measure to the considerable experimental difficulties in working with materials of such low conductivity. They are in fact insulators of rather high caliber. (10^{-16} , 10^{-18} mho/cm. resp.) The theoretical picture for electronic conduction in such materials is only now being partially clarified. It must meet the fact that, for example, carefully purified molten naphthalene has a 1000 fold higher electronic conductivity than does the solid single crystal original material^{117,131,132}, i.e., instead of the expectable drop of conductivity upon radically decreasing the crystalline order, one observes a large opposite effect.

Eley³⁵, Akamatsu³ and Garrett⁴⁶ have made reviews covering work on organic hydrocarbons. In addition there have been several contributions to work on the hydrocarbons in more recent years, such as that of Kearns and Calvin⁷⁰ on coronene, Wilk¹⁶⁶ on a long series of aromatic hydrocarbons, such as diphenyl anthracene, phenyl anthracene, phenyl phenanthrene, picene, and rubrene. Kuroda and Flood studied⁸³ meso naphthodianthrene, Lyons, Bree and Morris⁹³ studied a long series including tetracene, pentacene, anthanthrene, ovalene, etc. Kommandeur, Korinek, and Schneider⁸⁰ noted a coincidence between E_g for dark conductance and the threshold energy for optically excited photocurrents (wavelength at 1/100 peak photocurrent) for naphthalene and pyrene, i.e.

	E_g	$E_{\text{phot.}}$
naphthalene	3.7 eV	3.65 eV
pyrene	2.4 eV	2.61 eV

However, the correlation loses some of its significance on noting that the E_g value cited is that of Pick and Wissman¹¹⁶, a value later revised down to 1.50 eV, according to Riehl¹³², and unpublished work of Pick and J.A. Bornmann¹¹⁷. The high value apparently arose from conductivity measurements made over a narrow range below the melting point where traces of impurity seriously aggravate experimental difficulties. The problem apparently still remains open to clarification.

Kommandeur and Schneider⁷⁹ have recently studied conduction in bulk single crystal anthracene. They noted a slight field dependence of conductance. Kepler⁷¹ recently reported on careful measurements of the mobility of electrons and holes in single crystals of highly pure anthracene. The mobilities reported were rather surprisingly large, about 1 to 2 cm²/volt sec. Rosenberg¹³⁵ observed the cis form of beta carotene to have a lower temperature coefficient of conductance than the trans isomer. Pigon and Chojnacki¹¹⁸ studied photoconduction in an anthracene surface cell, and using the recent results of Lyons¹¹⁴ for the mobility ratio (holes to electrons) concluded that the tendency for hole trapping was not much greater than for electron trapping. Akamatsu, Inokuchi and Kuroda⁴ recently reported on the electrical conduction of thin films of aromatic compounds such as perylene, coronene, and violanthrene. Northrup^{111,113} also recently discussed carrier sources and conduction mechanisms in aromatic hydrocarbons.

In general it is to be observed among the aromatic molecules as a class the conductivity is higher the larger the molecule. The presence of heteroatoms such as nitrogen or oxygen also appears to enhance the electronic properties, such as conduction. There are many exceptions, however. The organic dyes studied so far seem to fall largely into two classes, the cationic dyes being n-type semiconductors, the anionic

dyes being p-type. The cationic dyes appear to be able to exist in two forms, one of which will induce photoconduction in the glass substrate below 10^9-10^{10} .

The organic free radicals form a curious group of compounds. The presence of an unpaired electron, as confirmed amply by paramagnetic experiments, confers unusual chemical properties. Judging from the few free radical (monomeric) compounds which have been studied so far, however, they do not appear to exhibit unusually large electronic semiconduction. Their conductivity appears to be rather 'normal' when one compares them with other non-radical molecules of related and aromatic structure. Data for the monomeric free radicals (as opposed to the high polymeric free radicals to be discussed later) are given in the table below.

THE CONDUCTIVITIES OF PURE FREE RADICAL COMPOUNDS

Substance	Specific Conductivity at room temp, mho/cm	Ref.
Violanthrene B (a nine ring aromatic compound)	10^{-6}	3,4
DPPH, diphenylpicrylhydrazyl	$10^{-8.9}$	3,4
Galvanoxyl ^a	10^{-13}	35
Phoxyl, Banfield and Kenyon's free radical ^b	10^{-15}	35

a: 2,6,3,5'-tetratertiarybutyl-4-methylene-2,5-cyclohexadiene-1 radical

b: 1,3 dimethyl-1,1-(phenylimine oxide)-butylidene-3-phenyl-N-oxynitrogen radical

The free radical polymers, however, are frequently observed to be quite conductive. This will be seen later in the discussion of the datively, covalently and ionic-ally bonded.

Among the monomeric molecules studied and which contain heteroatoms, are the phthalocyanines. The phthalocyanines, with and without sequestered metal atoms have been much studied^{30-1,74-5, 151-7}. These molecules are quite heat stable, showing little decomposition even at 500°C. The conductivities are not generally

high (about 10^{-8} mho/cm). There exists a particularly interesting observation by Kleitman⁷⁴ and by Haak and co-workers⁴⁹ that rectification can be obtained using phthalocyanine powder compacts and metallic electrodes. Haak et al showed that a film of polar material covering the crystallites is a necessary prerequisite for rectification. Sulfuric acid, nitric acid, or water in trace amounts provide such films, but acids such as HCl do not, indicating that oxidation may perhaps be involved. If the two metallic electrodes are different, the effect is more pronounced, suggesting that an oxide film of the least noble metal may be a factor in the rectification. Space charges may also be involved. Rectification factors of up to 500 have been observed at low frequencies (60 cps or less).

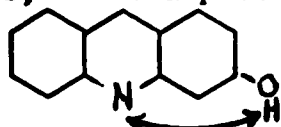
A significant observation as to the mechanism of conduction in organic films was made by Kuroda and Flood⁸³. They observed the effect of oxygen upon films of meso-naphthodianthrene (I) and of mesonaphthodianthrone (II), where conductivity of (I) increased upon exposure to air in a rather reversible fashion, and the virgin (I) shows a 'forbidden energy gap' E_g , of 0.74 eV, but the air exposed film showed 0.40 eV at low temperatures and 0.74 eV at high temperatures. They concluded that the low activation energy was to be associated with surface, the high activation with bulk conductivity, and considered that the sorbed oxygen atoms created new carriers. The diketone, (II), showed an activation energy of 0.43 eV at low temperatures and 0.73 eV at high temperatures, both measurements being done in vacuo. They suggest that oxygen sorbed on the surfaces of the hydrocarbon, (I) forms molecular complexes, creating unpaired electrons responsible for the observed sharp peak on electron spin resonance, and for the electronic charge carriers.

Wihksne¹⁴⁵ and Newkirk in an extension of the earlier work of Eley & Parfitt³² report finding that the alpha-form of phthalocyanine has a much higher conductivity than that of the

beta form, greater by a factor of 10^5 , and also possessed of a much lower activation energy, E_a (calc. from $\sigma = \sigma_0 \exp(E_a/kT)$). They observed E_a (alpha) = 0.25 eV, E_a (beta) = 0.9 eV, and could see a sharp electron spin resonance in the alpha form, but none in the beta. Incidentally, the temperature coefficient of the spin concentration did not match that of the conductivity, indicating that carriers were not linked one-to-one with determinable spins.

The conductivity of pure polycrystalline phthallic anhydride was found by a Polish worker, Heydel-Zyczkowska⁵⁹ to have the low value of $1-2 \times 10^{-18}$ mho/cm, with an apparent activation energy of 2.11 eV in the temperature range of 60-100°C, and 1.37 eV below 60°C. Htoo⁶¹ has made an extended investigation of over 100 white or colorless organic powders including saturated aliphatic compounds, unsaturated aliphatic compounds, mononuclear cyclic compounds, polynuclear cyclic compounds, heterocyclic compounds, monomers of polyelectrolytes, and various organometallics. His results were negative, as all were found to be insulators. Baba and Nitta⁵ observed a barrier layer with a surface potential of over 70 mV at the surface of phthalocyanines or crystal violet in photo-excitation experiments. They concluded the hole-electron pair produced by illumination recombined bimolecularly.

An interesting example of tautomerism in the solid state has recently been described²¹. Such materials may have electronic characteristics of considerable interest in memory devices, for example. The compound described is:



apparently capable of internally transferring a proton.

THE POLYMERS

Coordination Complex Polymers

It is possible to make highly conductive organic com-

plexes using electron donor-acceptor pairs extending throughout the medium to couple molecules such as the aromatic hydrocarbons. In terms of accepted polymer terminology, the functionality of most of the molecules present must be at least two in order to obtain long chain lengths.

Anthracene, which is an insulator, can be made to conduct by incorporating alkali metal atoms as complexes with it. Complexes such as these were studied by Ubbelohde and coworkers¹⁵⁰⁻¹, and shown to have conductivities of 10^{-8} to 10^{-11} as compared to that of the parent anthracene of 10^{-15} to 10^{-18} mho/cm. Akamatsu¹⁻⁴ and coworkers in Tokyo synthesized complexes of quite high conductivity, (up to 2×10^{-2} mho/cm) on using complexes of iodine with dibenzanthrone (violanthrene) and obtained similar results on related materials. Kommandeur and Hall⁷⁸ obtained conductivities of 10^{-1} mho/cm using perylene-iodine complexes. In England, Eley^{22,31-5} and coworkers, and in the United States, Labes and Sehr⁸⁴⁻⁵ have studied numerous complexes formed from aromatic donor-acceptor pairs of bifunctional nature, such as diamine-quinone complexes.

Labes and Sehr⁸⁴, for example, reported that the coordination complex formed by the bifunctional p-phenylene diamine and chloranil and in the form of polycrystalline pellets, had a specific conductivity of 10^{-8} mho/cm at 25°C and an activation energy, E_a , of 0.57 eV, as judged from conductivity-temperature data. It showed a Seebeck coefficient (thermoelectric power) of $Q = 1.1 \times 10^{-3}$ volts/°K (from -36°C to 49°C) a thermal conductivity of $K = 2.0 \times 10^{-3}$ watts/cm. deg., and a 'figure of merit' $Z = Q^2 \sigma / K = 10^{-11}$. From these values, assuming equations for the intrinsic semiconductor model, the reviewer calculates the mobility ratio, $c = u_e / u_h = 0.282$, the carrier concentration, $n_e = 7.0 \times 10^9 \text{ cm}^{-3}$ and the mobilities as $u_h = 7.0 \text{ cm}^2/\text{volt sec.}$, $\mu_e = 2.0 \text{ cm}^2/\text{volt sec.}$ One might suggest from this calculation that whereas the carrier concentrations were quite low, the mobilities are moderately high.

Imidazole, ... $\text{N}=\text{CH}-\text{N}-\text{H}\cdots$, which is a hydrogen bonded^{19,20} complex showed a conductivity of 10^{-10} mho/cm with an activation energy of about 1.4 eV.

There has been some assertion that the carriers in coordination complex polymers, such as the pyrene-iodine type, are to be identified 1:1 with the spin concentration measurable by techniques such as electron spin resonance⁷⁸, for in such materials there appears to be a close correspondence between the temperature coefficients of behavior, and the numerical count of carriers and spins. This interesting notion has not received much support from evidence in other materials, however. Studies by Smaller, Isenberg and Baird¹⁴¹ on indole-iodine complex showed no correlation between the temperature coefficients of the ESR and conductivity. Below a current density of 2×10^{-2} microamperes/cm², the resistivity was observed to be non-ohmic, following a $V = k \cdot I^{-0.8}$ relation. From ESR measurements, the magnetogyric ratio, $g = 2.0036 \pm 0.0006$. Studies by Leblanc and Huggins⁸⁸ on carotene-iodine complex similarly showed no 1:1 correlation between the conductivity, indicating that the conduction electrons were not to be identified strictly with the spins observed in ESR measurements. The complex, $\text{C}_{40}\text{H}_{56}\text{I}_3$, melts at 137°C, is green by transmitted light, red by reflected light, and has a conductivity of about 5×10^{-9} mho/cm at room temperature and an activation energy $E_a = 0.55 \pm 0.05$ eV. Again $g = 2.003$. Comparison with Coppinger's radical indicated a spin concentration of about 10^{19} cm⁻³, or about 0.01 to 0.02 spins per $\text{C}_{40}\text{H}_{56}\text{I}_3$ which appeared to change little with temperature. The spin signal decayed in air with a half life of about two weeks. It is to be concluded that either ESR is not a measure of the carriers, or that it may be, but that the mobility varies strongly and exponentially with temperature.

Recent work on the electronic characteristics of the coordination complexes included studies of the ESR absorption of biradical molecular complexes such as p-phenylenediamine-chloranil.^{17,23,62-3,100}

Coordination polymers incorporating metal atoms in the backbone chain have been made. Those made of alkali metal

atoms coordinated to hydrocarbons have already been referred to¹⁵⁰⁻¹. A stronger bonding is obtained between oxygen and metal atoms. Such polymers were prepared by Kanda and Kawaguchi⁶⁸, by reaction of CuSO_4 (aq.) to form 1,6 dihydroxyphenazinato Cu(II); (A): 2,5 dihydroxy p-benzoquinonato Cu(II); (B) and rubeanato Cu(II); (C). Conductivity measurements on (A) indicated a specific conductivity at 60°C of 10^{-13} mho/cm, $E_a = 1$ eV on using d.c. and a conductivity of 10^7 mho/cm on using a.c. Measurements on (B) were not very reproducible, but indicated a specific conductivity of about 10^{-10} on using d.c. and 10^{-7} on using a.c. The properties of (C) were more reproducible, indicating a conductivity of 4×10^{-6} , $E_a = 0.3$ eV on using d.c. and 2×10^{-6} , $E_a = 0.2$ eV on using a.c. It is not clear at present why the difference exists between the d.c. and high frequency a.c., and why the d.c. results give lower conductivities than the a.c. This does seem to be a particularly interesting area of study however.

The ferrocene complex polymers such as the ferrocene ketone and ferrocene benzal polymers (see later) described by Pohl^{14,127-8} et al are further examples of conductive coordination polymers with metal atoms in the main chain.

Covalency Bonded Polymers

Here we shall review work on the more conventional polymers such as those having main chain C-C or similar bonds. It is usual to obtain insulators from the conventional polymers such as the vinyls (polystyrene, polytetrafluoroethylene, polyethylene) or the condensation polymers (nylons, polyesters, etc.) Recently however, it has been shown that polymers with considerable conductivity can be obtained¹²⁰⁻³⁰. Typical of a large class of semiconducting polymers are the polyacene quinone radical polymers¹²⁸ (PAQR). These can be prepared by condensing various aromatic hydrocarbons and their derivatives with acidic molecules. Conductivities up to 0.01 mho/cm. were observed. Weiss and co-workers in Australia¹⁶²⁻⁴ have made polymers from phenols which they call xanthene polymers. Conductivities as low as 10^{-4} mho/cm

were observed in the xanthene polymers.

The PAQR polymers studied by the Princeton group in most cases are hard, black, cross-linked polymers showing a slight thermoplasticity. They can contain a high concentration of unpaired electrons, ranging from 10^{17} to 10^{21} spins/gm. The peaks are sharp and quite characteristic of free radical compounds, hence the term 'radical' in the provisional name of this class of polymers. The conductance follows the exponential temperature dependence,

$$\sigma = \sigma_0 \exp(-E_a/kT) = \sigma_0 \exp(-E_g/2kT)$$

The conduction and thermoelectric power behavior can be well fitted by equations of the usual type for intrinsic semiconductors, and simultaneous application of equations developed for thermoelectric power data by Johnson and Lark-Horowitz⁶⁵⁻⁶. The carrier concentrations and mobilities so calculated for several PAQR polymers are shown in Table I. The data fit this two carrier model quite well, but cannot be fitted by an impurity model assuming but a single carrier. It is to be emphasized that the 'fit' of conventional semiconductor equation based upon a simplified band model employing Bloch functions, and Lorentz-type modifications of the Boltzmann thermal distribution of electron momenta, does not prove that the assumptions of the model apply in the case of these non-crystalline polymers. In fact, in the realm of low mobilities, i.e., less than about $10 \text{ cm}^2/\text{volt sec.}$, the electron mean free path is already less than the thermal electron wave length (about 70 \AA), & the theory employing a notion of a mean velocity of a distribution of velocities of wave packets must be only an approximate representation of events. The matter is more fully discussed elsewhere¹²⁷. It seems clear that a hopping process model would better describe events in such materials.

The polymers prepared by the condensation of various substituted aromatic hydrocarbons with various aromatic acid derivatives (i.e. the PAQR polymers) conduct by electronic

TABLE I

Acene		Resistivity (ohm cm.)	Resistivity after SOCl ₂ treatment (ohm cm.)	Resistivity of ZnCl ₂ catalyzed PAQR (ohm cm.)
I & J	Biphenyl	9.1×10^{11}	(decomposed to tar) 10^4	3.4×10^{10}
C & D	Terphenyl	6.2×10^{11}	2.8×10^{11}	1.4×10^7
G & H	Naphthalene	1.6×10^{12}	6.7×10^{11}	1.4×10^6
A & B	Anthracene	1.5×10^6	2×10^9	3.2×10^5
E & F	Phenanthrene	7.8×10^{11}	4.9×10^{11}	1.0×10^5

TABLE II
Polymers of Quinones and Diisocyanates 129

Monomers		Temperature °C	Solidification Time (min.)	Total polymer- ization time(hr)	Resistivity
101	1,4 Naphthaquinone / TODI	100	no polymer		
102	1,4 Naphthaquinone / TODI	100	no polymer		
103	1,4 Naphthaquinone / TODI	250	15	18.25	4.6x10 ⁻¹¹
104	1,4 Naphthaquinone / TODI	250	15	1.25	2.5x10 ⁻¹¹
105	1,4 Naphthaquinone / TODI	250	15	.25	2.5x10 ⁻¹¹
106	1,4 Naphthaquinone / TODI	306	4	18 (min.)	5.9x10 ⁻¹¹
110	1,4 Naphthaquinone / TODI	306	4	4	6.7x10 ⁻¹¹
113	Anthraquinone / TODI	306	50	1	6.5x10 ⁻¹¹
114	Anthraquinone / TODI	306	50	19	6.2x10 ⁻¹¹
115	Paraquinone / TODI	256	23	18	5.6x10 ⁻¹¹
116	Paraquinone / TODI	306	8	18	4.7x10 ⁻¹¹

TODI = p - Toluenodiisocyanate

and not electrolytic means. This is shown by noting that the electrical properties remain unchanged upon passing many times enough coulombs of electricity to electrolytically plate out all atoms present. It is also shown by the fact that a Hall coefficient can be observed for such a polymer, and that the conductivity increases rather than decreases as pressure is increased. The semiconducting PAQR's can be either p-type or n-type semiconductors, as judged by the sign of the thermoelectric power. There is a small field dependence of the conductivity¹³⁰ corresponding roughly to $R = R_0 E^{-0.02}$, where R is the sample resistivity and E is the field strength.

A PAQR polymer has a chemical structure which is conducive to high electronic conductivity¹²⁹ and which can be destroyed, decreasing conductivity, by heating for long periods to about 500°C. Heating to higher temperatures, such as 800°C drastically lowers the resistivity for it then is converted to a pyro-polymer.

The conductivity of members of this class of polymers made from the same acidic component show the conductivity to be a fairly smooth function of the number of fused aromatic rings in the aromatic hydrocarbon portion of the molecule¹²⁹. This is a particularly interesting observation for it shows not only the trend which one would expect, but also signifies that since the conductivity of this series is seen to be structure dependent, other effects such as impurity or morphological differences must be relatively unimportant in such compounds. It, furthermore, gives hope that one can eventually 'molecularly design' organic semiconductors to an optimum specified set of characteristics.

Let us now turn to some other types of polymers having enhanced electronic properties. Those prepared by Pohl and Engelhardt, using Friedel and Crafts synthesis¹²⁹, from aromatic hydrocarbons and acid chlorides (see Table I) have conductivities ranging from 10^{-8} to 10^{-12} mho/cm. Condensation polymers¹²⁹ obtained by halogen extraction from 1,2,4,5 tetrabromobenzene

were reddish-black, and had low conductivities, about 10^{-11} to 10^{-12} mho/cm. Aniline black polymer¹²⁹, purified, had a conductivity of 3×10^{-11} mho/cm. Condensation polymers of the Schiff base type obtained from quinones and aromatic diisocyanates¹²⁹ (see Table II) had low conductivities.

Ferrocene polymers¹²⁸ can be insulating or semiconductors. Polyvinyl ferrocene¹²⁷ is an insulator, as might be expected by analogy with polystyrene. Upon incorporating the ferrocene molecule in structures accentuating electronic transfer, semiconduction can result. Linking the ferrocene groups with carbonyl groups^{103,127} gives materials ranging from 10^{-3} to 10^{-12} mho/cm. The more highly conductive material can exhibit rectification if placed between dissimilar (Ag-Pt) electrodes¹²⁷. Linking the ferrocene groups by benzal groups, $-\text{CH}(\text{C}_6\text{H}_5)-$, gives a material¹²⁷ with conductivity of $10^{-7,8}$ mho/cm. The latter two polymers have metal atoms coordinately bonded in the main backbone chain of the polymer, it will be noticed.

Polyphenyl¹²⁷ of moderate molecular weight exhibits a conductivity of $10^{-10,11}$ mho/cm.

Polytetrachlorophenylthioether¹²⁷ can be obtained in several forms. One with a conductivity of 1 mho/cm shows rectification between Ag-Pt electrodes, is infusible, and black. The form having a conductivity of about 2×10^{-7} mho/cm is thermoplastic and somewhat translucent.

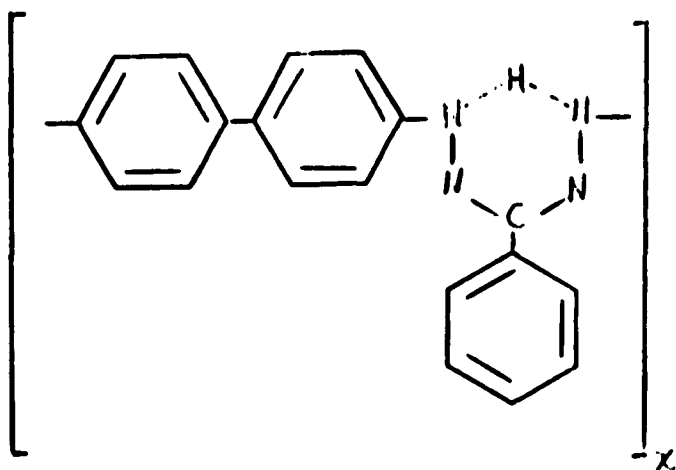
Copper phthalocyanine polymer exhibits moderately high conductivity (10^{-4} mho/cm³⁷; 10^{-8} mho/cm³⁹). The conductivity is rather higher than that of the monomer, $10^{-10,11}$ mho/cm.

Dehalogenation of existing polymers, such as polyvinylidene chloride yields semiconductive material. Abstracting HCl with bases such as NaOH or morpholine¹³ yields slightly conductive material, 10^{-13} mho/cm. Photochemical degradation by ultra-violet can induce semiconduction¹⁴. Heat treatment produces pyro-polymers with conductivities approaching that of

the metals. The higher the temperature of heat treatment the higher the conductivity, i.e.

T_H , °C temperature of heat treatment	Conductivity, mho/cm ⁽¹⁶⁷⁾
350	10^{-16}
394	10^{-12}
450	10^{-9}
800-1200	ca. 100 to 1000

Neoformazan, a slightly conductive polymer of high temperature stability⁴⁹ is reported as having a conductivity of $10^{-13,14}$. It is of the reported structure:



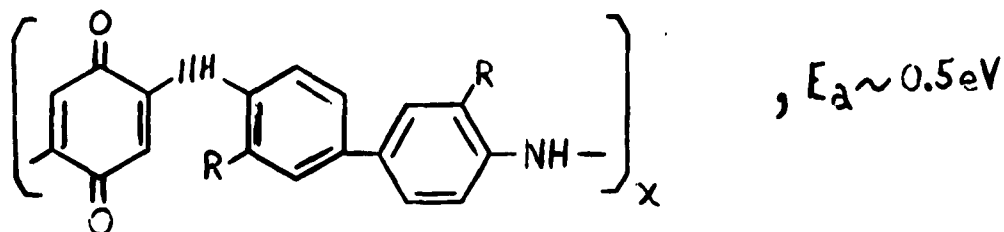
Berlin⁹⁻¹², in making a review¹⁰ of Russian work in the area of organic semiconductors, described several interesting polymer structures. The aryl substituted polyacetylenes were described as being abnormally stable, and quite inert to hydrogenation, bromination, or to addition of maleic anhydride or $SbCl_3$. Phenyl acetylene, upon being polymerized, exhibited a very low conductivity, about 3×10^{-19} mho/cm at room temperature, ($10^\circ C$) and an activation energy of conduction of about $2.2 \text{ eV} = E_a$. Upon heating to $300^\circ C$ the material altered and exhibited a room temperature conductivity of 3×10^{-16} mho/cm with $E_a = 1.4 \text{ eV}$. The

spin concentrations ranged from 10^{17} to 10^{18} gm^{-1} . The existence of biradicals was suggested to account for this.

Polymers with heteroatoms in the main chain were emphasized. Among those described were:

a) polyphenyleneazo compounds, $\left[\text{C}_6\text{H}_4\text{--C}_6\text{H}_4\text{--N=N--} \right]_x$, $E_a \sim 0.8 \text{ eV}$

b) polyphenyleneaminoquinones, which can chelate metal atoms within them.



Besides a narrow line EPR, there is a wide line peak of about 500 to 600 oersteds half width, corresponding to 10^{21} to 10^{23} spins/gm.

c) polyphthalocyanine-metal surface compounds formed by heating tetracyanobenzene in contact with copper or iron. Such materials were reported to show conductivities of about $2.5 \times 10^{-2} \text{ mho/cm}$, with $E_a = 0.13 \text{ eV}$.

d) polymeric complexes of percyanoethylene, characterized by high values of dielectric constant and magnetic susceptibility ($X = 60 \times 10^{-6}$), and electrical conductivity of 10^{-2} mho/cm with $E_a = 0.21$ to 0.26 eV .

It appears that a covalently-bonded polymer can form complexes with small molecules to give material of higher conductivity. An example of this is the complex of iodine with poly-N-vinyl-5-methyl-2-oxazolidinone¹²⁷. The original materials have conductivities of 1.9×10^{-10} and 10^{-44} mho/cm respectively. The complex exhibits a conductivity of about $2 \times 10^{-7} \text{ mho/cm}$, if dried in the presence of excess I_2 vapor.

Among the hydrogen-bonded polymers, the proteins and polypeptides have been studied by Riehl¹³³ and by Eley³⁵⁻⁶ and co-workers. Eley observed that the strongly dried materials

had conductivities of 10^{-12} to 10^{-20} at 400°K , with temperature coefficients, which they interpret as 'energy gaps' ranging from $E_g = 2.57$ to 3.12 eV. Riehl, examining proteins which had not been so intensively dried, and which still contained about 0.6 mole $\text{H}_2\text{O}/100$ g of dry protein, corresponding to 2 to 3 molecules of water per amino acid group, observed conductivities of about 10^{-10} mho/cm, and a temperature coefficient $E_a = 0.9$ eV. This behavior corresponded to that of ice. He therefore concluded that transport in this instance was by means of the hydrogen bridges, and ionic in nature.

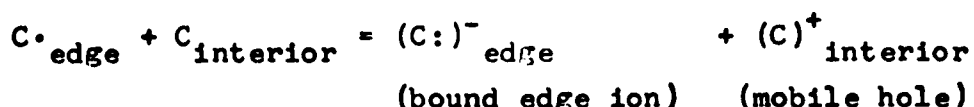
Polyelectrolytes which conduct in non-aqueous media (e.g., benzene) have been prepared by Wasserman, French and Roubinek¹⁶⁰⁻¹. This type of electrolytic conduction in hydrocarbon solutions, as by various organic salts, is well known from the work of Kraus⁴⁴. The electrolytically conducting polymers described by Wasserman et al were prepared from cyclopentadiene derivatives, and were generally studied as the trichloroacetic acid salt. Their conductivity in the solid state has not as yet been reported.

Pyro-Polymers and Polymer Carbons

Pyro-polymers and polymer carbons are classes of easily prepared semiconductors which can be made to be as conductive as some metals. They are prepared by heating any of a wide variety of organic substances to elevated temperatures. Pyro-polymers are distinguished from the polymer carbons as being made at lower heat-treatment temperature, T_H , and more important, containing appreciable fractions of atoms such as H, O, other than carbon. It is customary to draw the line of distinction at $T_H = 1200-1300^\circ\text{C}$ where the pyrolysed material contains approximately 1 mole % or less of atoms other than carbon.

Electron spin resonance studies show that the pyro-polymers contain free radicals in great number at heat-treatments of up to 650°C and that they disappear on further heating, but

the conduction becomes quite high. It seems likely that the free radicals are formed at the edges of large condensed ring structures, and that as the ring structures grow larger as higher heat treatment continues, increased ease of abstraction of the π electrons from the ring structures occurs. This converts the edge radicals to bound negative ions, forming conductive valency holes in the ring structures.. There is further the possibility that the ring structures themselves can exhibit internal dissociation to form mobile holes and electrons. The reactions may be simply represented as:



and



The effect of including atomically distributed metal atoms as dopants has been studied^{86,110-4}. The principal effect appears to be to change the mobility of the carriers in their hopping from stack to stack of the ring structures. Mobilities as high as 120 cm²/volt second have been observed¹²¹.

The pyropolymers can be prepared to have the highest conductivities of any class of organic materials so far examined. (greater than 1000 mho/cm on occasion). As such they must, of course, be examined theoretically in terms of degenerate semiconductors or semi-metals. The high temperature of preparation suggests that they should have a high use temperature. They can be prepared as very hard or very soft materials¹⁷⁴. Recently F.C. Cowlard at Plessey Ltd. has prepared non-porous pyro-polymers and polymer carbons characterized by high conductivity and inertness. They are promising materials for high temperature containers useful in preparing other semiconductors.

Pyro-polymers made from organic polymers or monomers which contain atoms such as N, O, Cl, Si, and S, etc., occasionally form semiconducting materials at rather low temperatures (T_H). Semiconduction is seen in the pyro-polymer obtained from such polymers as polyacrylonitrile^{127,147}, polysaccharides⁷⁶, or polyvinylidene chloride¹⁶⁷⁻⁷² by heating at the relatively low temperatures of 400-600°C. It has been suggested, for example, that in the case of polyacrylonitrile, the material can undergo a ready internal rearrangement to form extensive conjugation as follows:



Impregnation of the polyacrylonitrile powder with metallic salts prior to pyrolysis can yield highly conductive solids, some of which are thermoplastic and translucent, or of light color¹²⁷. Topchiev¹⁴⁷ et al prepared semiconducting pyro-polymers of polyacrylonitrile in powder and in fibrous form. CuCl_2 impregnated material was reported as having a conductivity of 10^{-2} mho/cm at 300°C. ESR measurements indicated g -factors of 1.981 to 2.001 (i.e. $\Delta g < 0$), a wave half width, characterizing the relaxation period, of 10 to 20 gauss, and spin concentrations of 1.7 to 15×10^{18} per gram. Pre-irradiation by gamma rays was reported to increase the spin concentration in the pyrolysed material.

Pyro-polymers made from polyacrylonitrile, from polyphenylene, and from nigrosine base NB were studied by Brown and Aftergut¹⁸⁻²⁰, following heat treatment at 470-500°C. They reported very low conductivities, less than 10^{-13} mho/cm for their materials, and reported unusually high 'energy gap' values with double values. This may reflect their method of measurement, which employed using polyethylene binder in making the specimen discs.

Winslow¹⁶⁷⁻⁷² et al made a detailed study of pyro-polymers obtained from cross-linked polyvinylidene chloride, pre-oxidized

polydivinyl benzene, and pre-chlorinated polydivinyl benzene. Akamatsu described several pyro-polymers⁴ and other Japanese workers reported semi-conducting pyro-polymers were obtained which contained silicon^{51,175} as well as carbonaceous materials. A U.S. patent describes material¹⁷⁴.

Kmetko⁷⁶ made an important observation on a series of differently pyrolysed cellulosic films, noting that the activation energy for conduction processes, E_a , if expressed as $2 E_a = E_g$, the 'forbidden energy gap' was in good agreement with the energy observed at the infrared cutoff frequency. Table III summarizes his findings. Some progress in explaining the course of conduction events in the pyro-polymers has been made by studies on the effects of metallic doping the pyro-polymers. It proved fruitful to consider the existence¹²¹ of carrier 'domains'. The carriers of either sign have a transitory existence, each roving about until it is captured by an oppositely charged particle and either being scattered or annihilated. The domain in which it moves until its demise can be considered to be proportional to the cube of its mobility. The domain is a property of the semiconductor. The 'effective' concentration of a carrier, n_e^* or n_h^* , as far as the capture processes for electrons and holes respectively are concerned are:

$$n_e^* = n_e (D_e/D'_e) \quad ; \quad n_h^* = n_h (D_h/D'_h)$$

where n_e and n_h are the actual concentrations of carriers, and D_e/D'_e and D_h/D'_h are the ratios of the domains of the carriers (electrons and holes, resp.) in the presence and absence of impurity. The n^* 's may be looked upon as the 'activities' and the D/D' ratios may be regarded as activity coefficients to the real concentrations, n_e and n_h . One would then expect

$$n_e^* n_h^* = K^* = n_e n_h (D_e/D'_e) (D_h/D'_h)$$

TABLE III

Comparisons of the Forbidden Energy Gap Obtained
by Optical Absorption Band Edges and by Thermal
Coefficients of Conduction for Cellulosic Pyro-
Polymer Films

<u>Heat treatment Temperature, °C</u>	<u>E_g, in eV, from conductivity</u>	<u>Mid Point of Transparency, eV</u>
300	--	1.2
350	--	0.87
425	0.8	0.71
500	0.62	0.50
540	0.41	0.33
630	0.22	0.28
700	0.09	0.2
800	0.03	--

and if degeneracy is not excessive, expect K^* to be relatively constant. The effect of high degeneracy upon K^* has been discussed by A.J. Rosenberg¹³⁴. A further expectation of the domain approach is that $D'_e/D'_h = D_e/D_h \approx c^3$, where c is the mobility ratio. It can be argued that the domain size should depend upon the impurity concentration, N ,

$$dD = kD dN$$

leading to

$$n_e n_h = K^* \exp(-2kN)$$

and

$$n_e n_h = K^*_o (\mu'_h/\mu_h)^6$$

where the μ 's are the hole mobility in the pure and impure materials. Both expectations appear to be at least roughly met by the data available to date.¹²¹

The formation of the pyro-polymers, and their next of kin, the polymer carbons, and in turn their ensuing relations, the pyrolytic graphites⁷³ may be considered to proceed in the following general fashion. During the heating of the organic precursor compound there occurs a fusion of the carbon atoms skeletons to form large highly aromatic structures. As the heat treatment temperature is increased, the ring assemblies become larger and form large net-like planes of atoms stacked in random arrays much like the bag of assorted coins. Order along the c axis is good, that along the a and b axes is usually poor in each stack until at very high temperatures (about 3200°C) the stacks may fuse into large sheets of rather high order, yielding graphite. The polymer carbons generally prepared at T_h between 1200°C and 2700°C have high conductivities, (about 20 to 1000 mho/cm). They are degenerate semiconductors with a narrow forbidden energy gap, about 0.07 to 0.01 eV in height. The heat treatment temperature, T_h , is a critical parameter in their preparation. The polymer carbons, as judged by the Seebeck coefficient⁹⁰⁻¹ sign, vary in dominant carrier type depending upon T_h , being n -type (at room temperature)

for $T_h = 1200-1700^\circ\text{C}$, changing to p-type for $T_h = 1700-2200^\circ\text{C}$ and reverting to n-type for $2200+^\circ\text{C} = T_h$. Mrozowski and co-workers^{90-1,105-8} have proposed a satisfying explanation for this odd behavior. They suggest, quite reasonably, that it is due to the role played by edge carbon atoms in abstracting pi electrons from the aromatic nets, forming edge carbanions, and free holes¹⁴⁹. The reversal of apparent carrier type is postulated as due to the shallowness of the band gap, initial losses of electrons showing as holes, further losses showing as electrons in a conduction band. Coulson²⁶ has recently elaborated upon the expected behavior of edge carbon atoms of such large aromatic networks remarking that three types of electronic bonding situations can be expected. Carbon atoms exposed as pairs at the edge can acquire a partially triple-bond character. Those exposed as lone 'points' can be expected to acquire a divalent s^2p^2 character. 'Tails', remaining from detached hydrocarbon residues for example, which are not incorporated within the aromatic ring, but which remain peripheral, can show unpaired electrons. The latter type, it would appear, could well be expected to form carbanions by abstracting the more loosely bound pi electrons from the aromatic network, leaving wandering holes.

On considering the enhanced electronic properties of the various organic materials observed so far¹¹⁵ one can draw up a number of rules:

- (1) Those molecular structures which permit a maximum of electron orbital interlap between neighboring molecules favor high mobility, high carrier concentration and high conductivity, e.g. ion-radical salts. There is some evidence that hydrogen bonding accentuates electronic conduction.
- (2) Those molecular structures which bring about a lowering of the excitation energy required to produce excited singlet or triplet electronic states accentuate conductivity.

- (3) Increase of size of the contiguous region of conjugation enhances conduction.
- (4) The presence of two or more single bonds in series between the more conjugated or aromatic portions of a molecule drastically reduces the conductivity. Compounds with such structures are generally insulators, with conductivities less than 10^{-12} mho/cm.
- (5) The inclusion of atoms other than C, H, or O often appears to enhance the conductivity.
- (6) In the same organic compound, the liquid state is more conductive than the crystalline solid state.
- (7) Electronic conductivity is high only in very dark or black compounds.

Considerations of these rules have led to another approach in dealing with polymeric organic semiconductors.

As an alternative to the simple band model approach in considering the semiconducting polymers, Pohl and Engelhardt¹²⁹, have used the following working hypothesis. There is now appreciable evidence that when the size of a set of conjugated double and single bonds is larger than some number (about 10 to 15 double-single bond pairs) then the molecule acquires unusual characteristics. It is to be expected that the formation of the biradical state (exciton) will then become easy. For ease of reference they have termed this required degree of conjugation as eka-conjugation. Eka-conjugation may be said to exist when the degree of conjugation becomes such that the extent of biradical (or similar exciton) formation becomes appreciable at room temperature. The energetics of the transition may be semi-quantitatively considered by the 'electron-in-a-box' model. Representing the biradical as $\cdot R \cdot$, and its eka-conjugated precursor as R , we may write



$$(2) (.R.)(R)^{-1} = K_1 = \exp(-\Delta F_1/kT)$$

$$(3) \Delta F_1 = \Delta H_1 + T\Delta S_1 \approx {}^3E$$

where 3E is the energy of conversion to the triplet state bi-radical. From the electron-in-a-box model, we may set as a fair approximation,

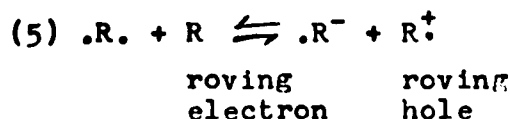
$$(4) {}^3E \approx E_{n=2} - E_{n=1} = \frac{\pi^2 \hbar^2 (n_2^2 - n_1^2)}{8ma^2}$$

$$\approx \frac{14.42}{x^2} ; \text{ (in eV) where } a = 1/2(2L_e x) = L_e x$$

$$L_e = \text{C}-\text{C bond length} = \text{ca. } 1.40 \text{ \AA}$$

$$x = \text{number of mers}$$

The ion pair forming reaction from which the carriers result may be written:



$$(6) \frac{(.R^-)(R^+)}{(.R.)(R)} = K_2 = \exp(-\Delta F_2/kT)$$

By this argument, we will expect to have an "intrinsic-type" semiconductor where

$$(7) (.R^-) = (R^+) = n_e = n_h = n_1,$$

and we may set $(.R.) = s/2 = 1/2$ the concentration of observable spins per cm^3 .

Combining we get:

$$(8) 2 n_1^2 / s(R) = K_2$$

$$(9) n_1 = (s/2) \exp \left[\frac{(-\Delta F_2 + \Delta F_1) 2kT}{({}^3E) kT} \right] \approx (s/2) \exp \left[\frac{(-\Delta F_2 + {}^3E) kT}{({}^3E) kT} \right] \\ = (R) \exp \left[\frac{(-\Delta F_2 - \Delta F_1) kT}{({}^3E) kT} \right] \approx (R) \exp \left[\frac{(-\Delta F_2 - {}^3E) kT}{({}^3E) kT} \right]$$

where n_1 is the number of either mobile electrons or mobile

holes acting as carriers.

As discussed elsewhere at greater length¹²⁷ there is reason to expect the mobility to occur by way of hopping processes, where E_s is the saddle height energy for the hopping process, and

$$(10) \mu = (\text{const.}) T^2 \exp(-E_s/kT)$$

In the event that there is a cooperative process between the carriers and excitons, a factor of $(n_{ix}/n_1 + n_{ix})$ must be included, and the new $E_s' < E_s$. Recalling that the eka-conjugated structures are large and assymetrical, as well as highly polarizable, it will be expected that some field dependence of the conductivity will result. The eka-conjugation model appears to account qualitatively and occasionally semiquantitatively for the various attributes previously mentioned for the PAQR polymers. Further study of this interesting area is actively in progress.

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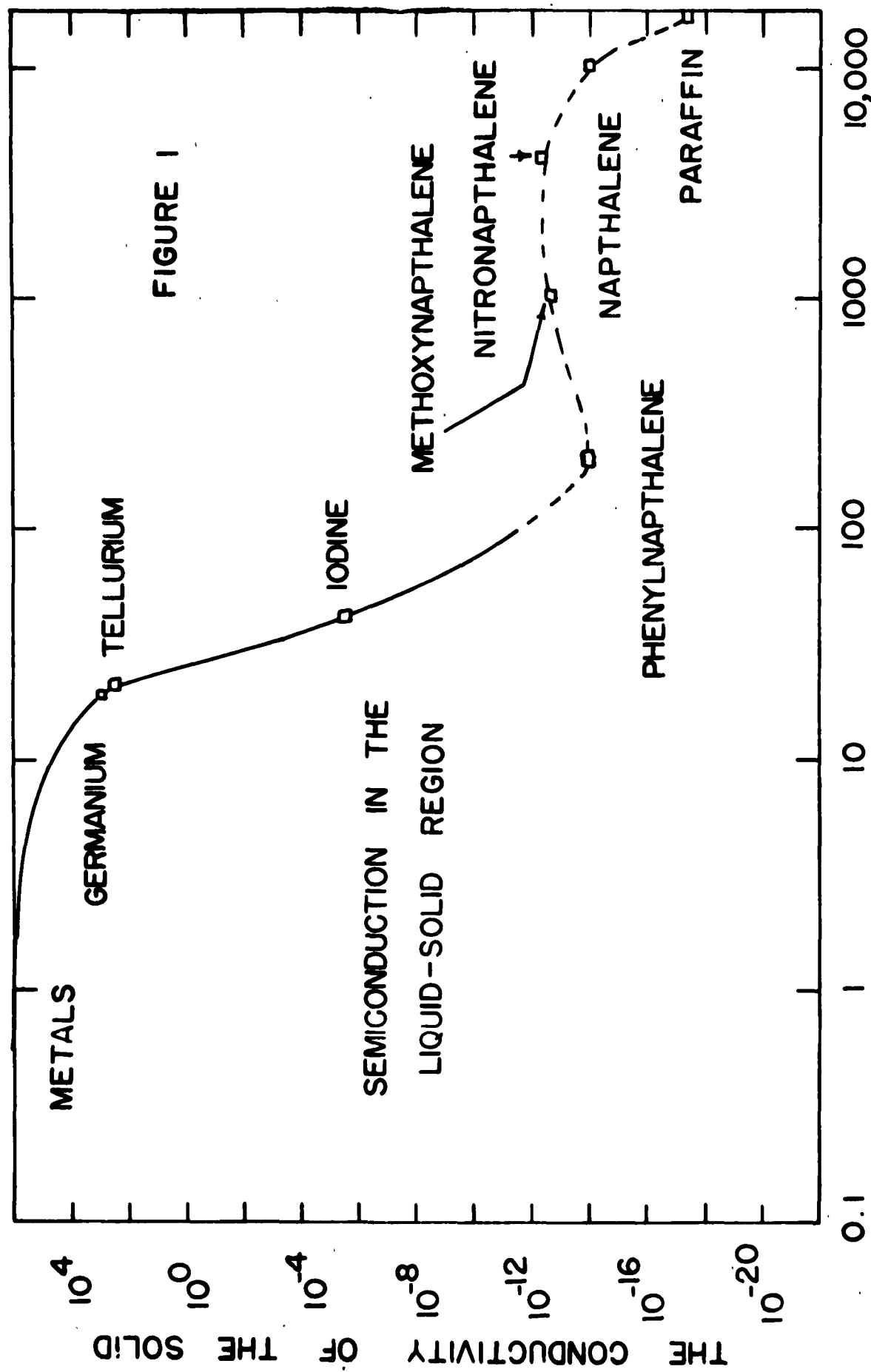
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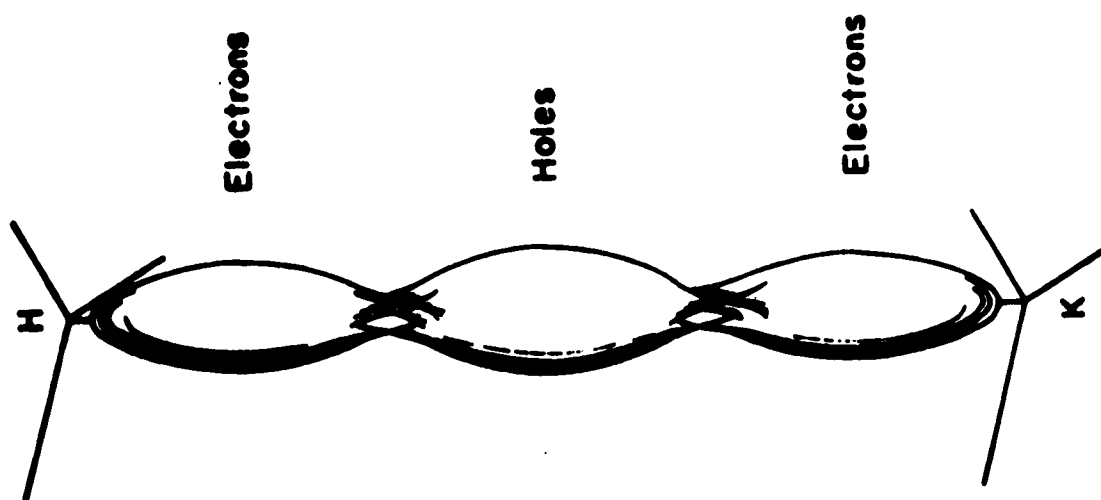


Figure 3

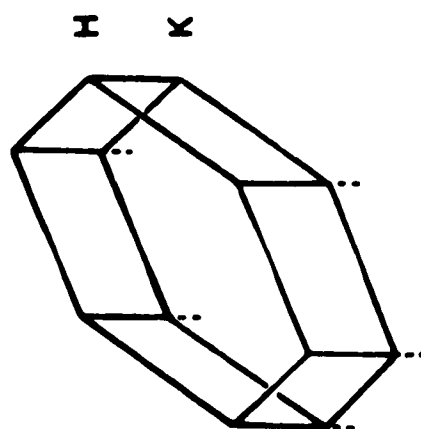


Figure 2

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